Supporting Information

Quasi-zero-dimensional cobalt-doped CeO_2 dot on Pd catalysts for alcohol electrooxidation with enhanced poisoning tolerance

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Experimental details

Figure S1 to **S9.**

Experimental Section

Chemicals. Palladium chloride ($PdCl_2$, ⩾99.0 %), ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$, ⩾99.0 %), tris(2,4-pentanedionato)cobalt ($Co(C_5H_7O_2)_3$, ⩾98.0 %), oleylamine ($C_{18}H_{37}N$, ⩾ 98.0 %), 1-octadecene ($C_{18}H_{36}$, ⩾95.0 %), ethylene glycol ($C_2H_6O_2$, ⩾ 99%), and PtRu (Pt 40%, Ru 20% mass loading) were purchased from Johnson Matthey® and used as received. Activated carbon (Ketjenblack®ECP-600JD) was purchased from Lion Corporation. All the solutions were prepared using deionized water.

Synthesis of Co-doped CeO_2 Dots. The Co-CeO_2 dots were prepared by a facile thermal decomposition method. Typically, 0.548 g (1.0 mmoL) ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) and 35.6 mg (0.1 mmoL) cobalt (III) acetylacetonate ($Co(C_5H_7O_2)_3$) as the cerium oxide precursor, 2.46 mL oleylamine as the capping agent, and 20 mL 1-octadecene as the solvent were homogeneously mixed by magnetic stirring under argon gas atmosphere. The mixture was then heated to 180 °C, kept for 2 h, and cooled down to room temperature. The Co-CeO_2 dots were collected via high-speed centrifugation (9000 rpm for 10 min), and washed with abundant hexane and ethanol successively. Finally, the clean Co-CeO_2 dots were dried in the vacuum oven at 80 °C and kept sealed.

Synthesis of catalysts. The Pd/Co-CeO_2 catalyst with 20 wt% Pd loading was prepared by a microwave-assisted ethylene glycol (EG) reduction method.[1, 2] Briefly, 10 mg Co-CeO_2 dots and 30 mg activated carbon powder were thoroughly mixed in 40 mL EG and 10 mL isopropanol mixed solution via rigorous stirring and ultrasonic treatment, then 9.4 mL 0.01 M $PdCl_2$ solution was added drop-wised into the mixture under extreme stirring. The solution was placed in an ultrasonic bath for 6 h and the pH value was adjusted to 10.0 using 1.0 M NaOH solution. Argon gas was bubbled into the mixture for 30 min to remove the dissolved oxygen, and the mixture was then heated in a microwave oven (2450 MHz, 800 W) for 90 s to reduce $PdCl_2$ into Pd dots. After cooling the mixture down to room temperature, the pH value of the mixture was adjusted to 4.0 by 0.1 M HNO_3 solution to assist the deposition of the Pd dots onto the carbon support. Finally, the Pd/Co-CeO_2 catalyst was separated by filtration and washed with water and ethanol several times. Before use, the Pd/Co-CeO_2 catalyst was dried at 80 ℃ in a vacuum for 10 h. The Pd and Pd/CeO_2 with 20 wt % Pd loading each were also prepared through the same procedure, except that CeO_2 dots were employed to replace the Co-CeO_2 dots. The Pd mass loading of the catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 8000DV, PerkinElmer), and the Pd mass loading of the Pd, Pd/CeO_2, and Pd/Co-CeO_2 catalysts were estimated to be 18.4 wt%, 19.0 wt% and 18.7 wt%.

Structure and Surface Conditions Analysis. Structure analyses were carried out by XRD, TEM, and HRTEM. The XRD was implemented by Panalytical X'Pert powder diffractometer. X-ray diffraction with Cu Kα radiation operating at 40 kV and 40 mA over the range of 20~90°. The XRD samples were prepared by depositing the precipitated samples on a silicon plate. The TEM and HRTEM measurements were performed using JEM2100 microscopes operating at 200 and 300 kV, respectively. Specimens were prepared for TEM by making suspensions of the catalyst powder in ethanol, using an ultrasonic bath. The suspensions were dropped onto clean holey carbon grids, which were then dried in the air at room temperature. The dot size distributions and average diameters of CeO_2 dots and Pd dots were determined from three different regions of the catalysts; each region contained more than 100 dots. X-ray photoelectron spectroscopy (XPS) was performed on a physical electronics PHI model 5700 instrument (Al Ka radiation).

Electrocatalytic Measurements. The electrochemical tests were performed in a three-electrode system controlled by a CHI workstation (CHI Instruments, Inc.) with Pt grid and Hg/HgO as the counter electrode and reference electrode, respectively. The performance of the synthesized catalysts was determined via glassy carbon electrode, and it was prepared by coating 15 μL catalyst-ethanol ink (5 $mg_{catalyst}$ 5 mL^{-1}) on the surface of a glassy carbon electrode (Φ=4 mm). Pd loading was 3 μg. After drying at room temperature, 5 μL Nafion ethanol solution (1 wt%) was dropped on the surface of the catalyst to form a protective film. Before testing, an argon flow was bubbled into the test system to remove the oxygen. The working electrode was first activated in 1.0 M KOH solution by cyclic voltammetry (CV) (-0.8~0.3 V with Hg/HgO reference electrode at 50 $mV\cdot s^{-1}$) until a steady CV curve was obtained. The electrocatalytic activity and durability of the MOR and EOR was measured using another three-electrode system which contained methanol and ethanol solutions with CV and chronoamperometry (CA). The mass activity (normalized with the mass of Pd loading) and special activity (normalized with the EASA of each catalyst) were applied to evaluate the activity of each catalyst. CO stripping tests were employed to evaluate the ability of various catalysts to tolerate poisoning in CO saturated 1 M KOH solution.

Additional Results and Discussion.

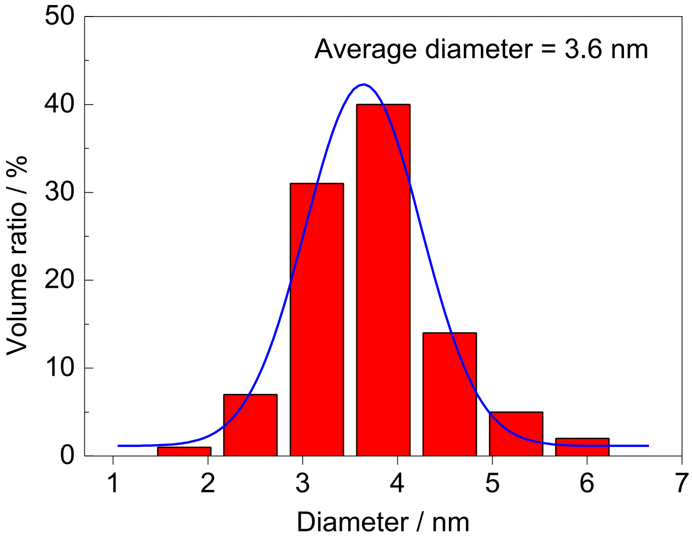
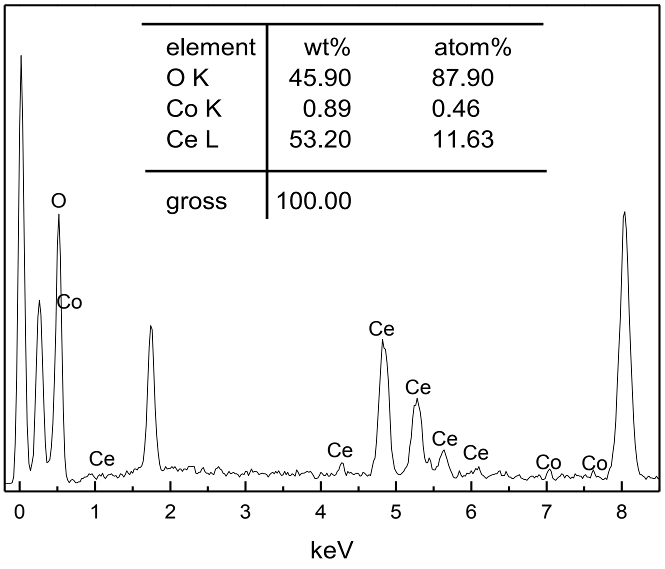


Figure S1. The histogram of the diameter distribution of the Co-CeO$_2$ dots.



element	wt%	atom%
O K	45.90	87.90
Co K	0.89	0.46
Ce L	53.20	11.63
gross	100.00	

Figure S2. The EDS result of Co-CeO$_2$ dots.

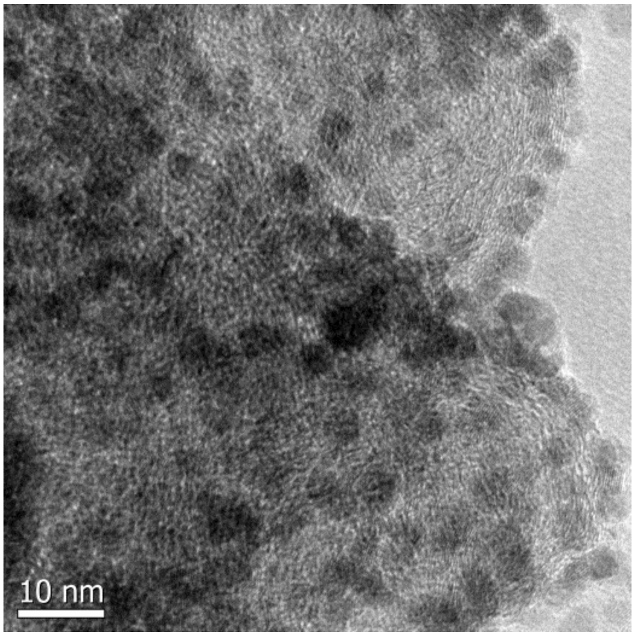


Figure S3. TEM image of the Pd/CeO_2 catalyst.

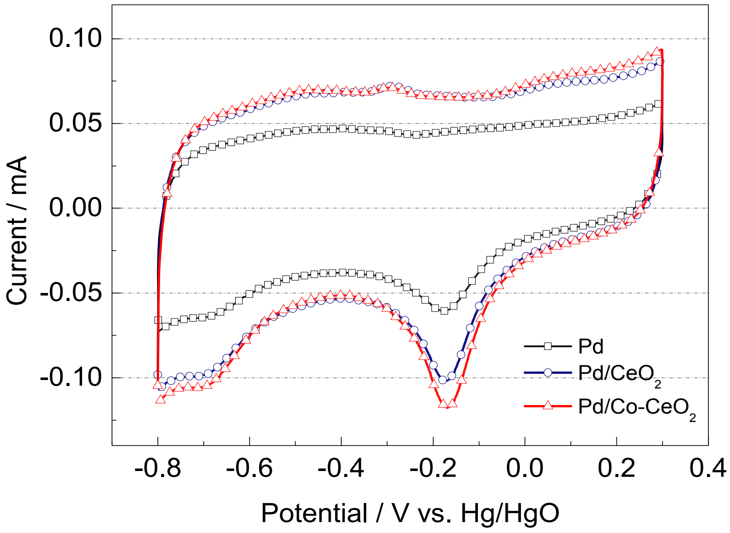


Figure S4. The cyclic voltammogram curves of the Pd, Pd/CeO_2, and Pd/Co-CeO_2 catalysts in 1 M KOH solution. Scan rate: 50 mV·s^{-1}, Sweep range: -0.8 V~0.3 V (vs Hg/HgO).

The electrochemical active surface areas (EASA) of various catalysts were measured by integrating the charges of the PdO reduction peak for the CV in a potential range of -0.8 V to 0.3 V at a scan rate of 50 mV·s^{-1} in 1 M KOH solution, and the calculating equation is as follows (**Equation S1**)[3]:

$$EASA_{Pd} = \frac{Q}{405\mu C \cdot cm^{-2}} \quad (1)$$

Where Q represents the electric quantity which is calculated by integrating the charges associated with the PdO reduction peak.

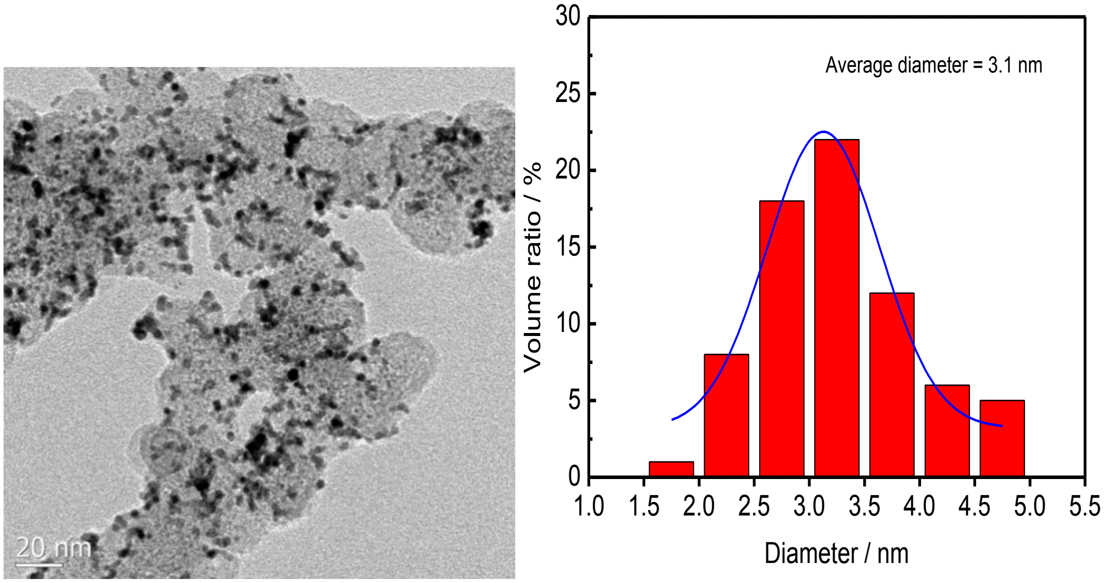


Figure S5. The TEM image and average diameter histogram of the PtRu catalyst.

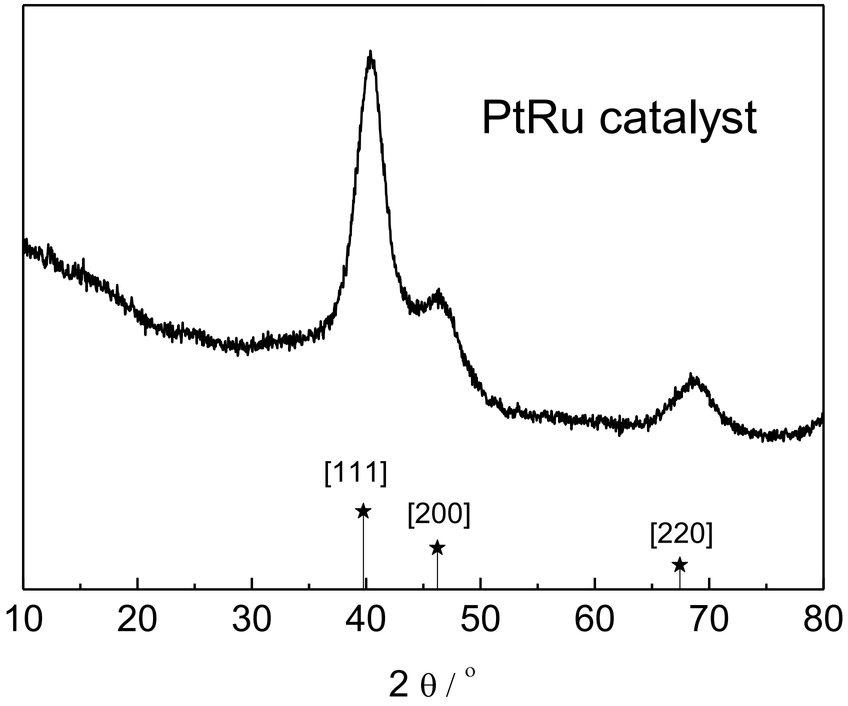


Figure S6. The XRD diffraction of a PtRu catalyst.

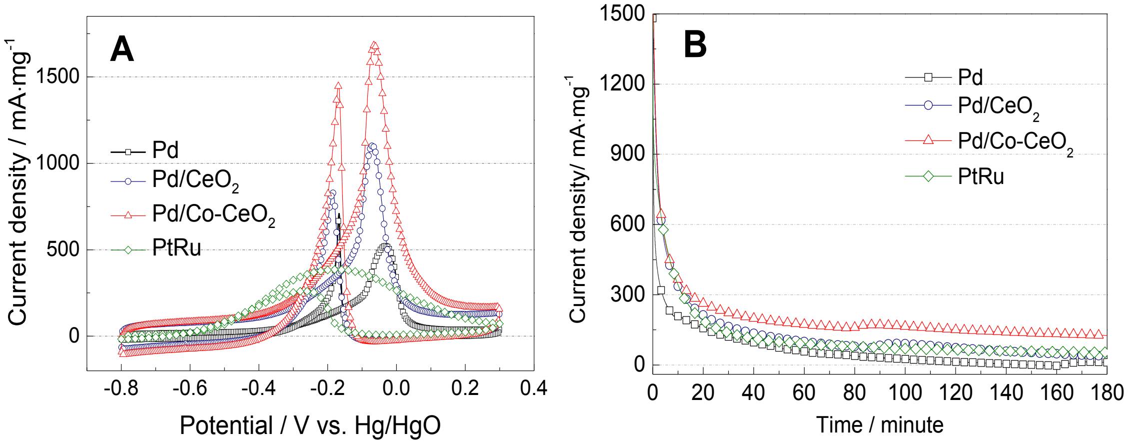


Figure S7. (A) CV and (B) CA curves of Pd, Pd/CeO$_2$, Pd/Co-CeO$_2$, and commercial PtRu electrocatalysts in 0.5 M C_2H_5OH and 1.0 M KOH mixed solution. Scan rate: 50 mV·s^{-1}, Sweep range: -0.8 V~0.3 V (*vs*. Hg/HgO). The current density is normalized by the mass loading of Pd and Pt.

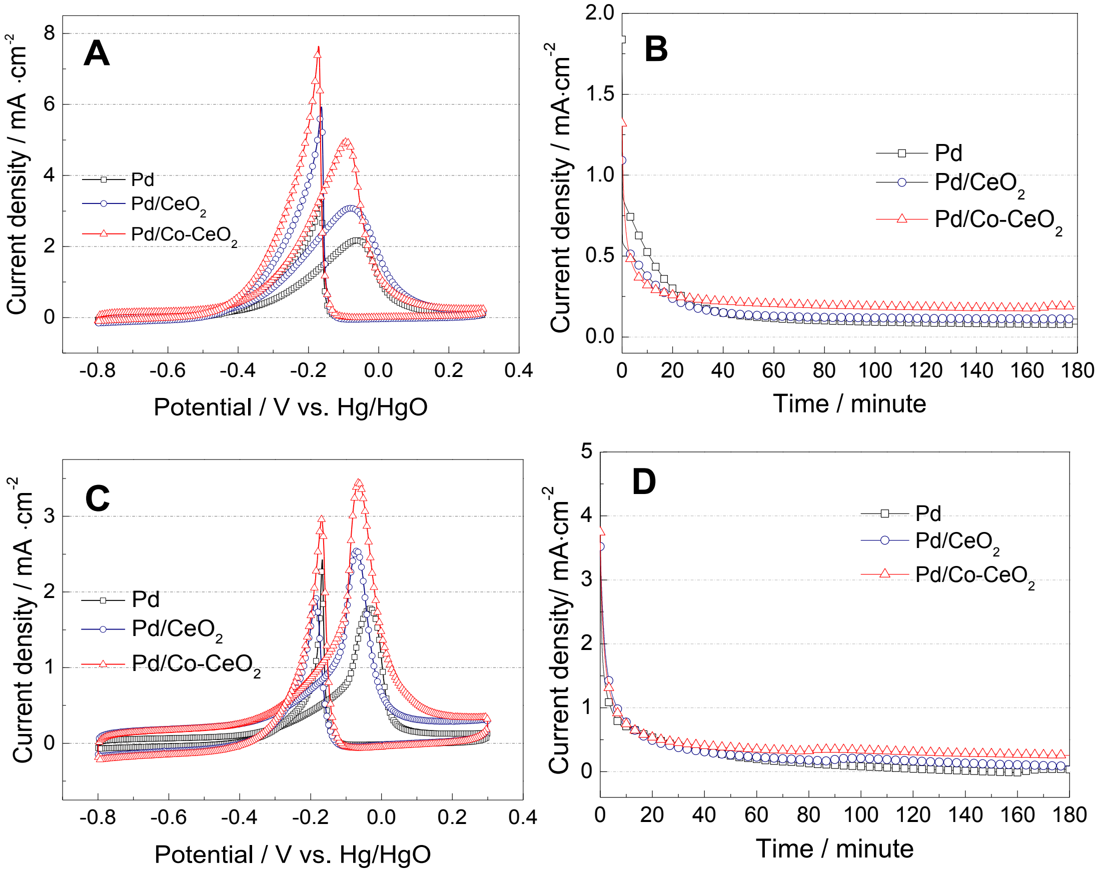


Figure S8. The (A) CV and (B) CA curves of the Pd, Pd/CeO_2, and Pd/Co-CeO_2 electrocatalysts in 0.5 M CH_3OH and 1.0 M KOH mixed solution; The (C) CV and (D) CA curves of the Pd, Pd/CeO_2, and Pd/Co-CeO_2 electrocatalysts in 0.5 M C_2H_5OH and 1.0 M KOH mixed solution. The current density is normalized by the EASA.

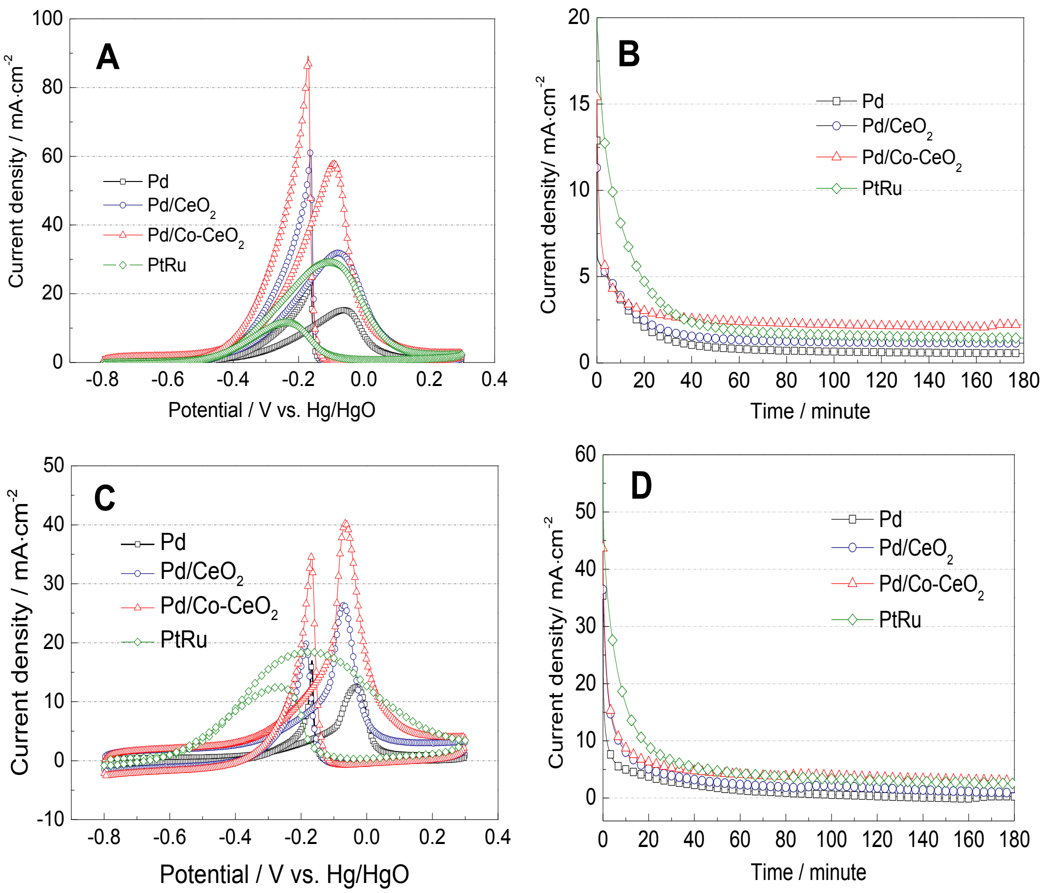


Figure S9. The CV and CA curves of the Pd, Pd/CeO$_2$, Pd/Co-CeO$_2$, and PtRu, electrocatalysts in 0.5 M CH_3OH and 1.0 M KOH mixed solution (A and B) and in 0.5 M C_2H_5OH and 1.0 M KOH mixed solution (C and D). The current density is normalized by the electrode area.

REFERENCES

1. Y. Sun, C. Du, M. An, L. Du, Q. Tan, C. Liu, Y. Gao and G. Yin, *J Power Sources*, 2015, **300**, 245-253.
2. Q. Tan, C. Du, Y. Sun, L. Du, G. Yin and Y. Gao, *Nanoscale*, 2015, **7**, 13656-13662.
3. R. Pattabiraman, *Applied Catalysis A: General*, 1997, **153**, 9-20.